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Spatial variability and temporal evolution of dissolved trace elements in the waters of the Venice lagoon (Italy)

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Abstract
A comprehensive dataset on dissolved trace element concentrations spanning a decade (2008-2017), collected during monitoring campaigns, is the result of an in-vestigation meant to evaluate spatial variability and temporal evolution in the Ven-ice Lagoon waters. The concentration levels at the different sites unfold that the la-goon is not homogeneous but a system of various parts having different characte-ristics affected by various pollutant sources, meanwhile the analysis for trend per-formed both at each site and at the entire lagoon as a whole revealed that arsenic and heavy metals showed little variations or decreasing trends, with the exception of iron that may have had an overall increase in concentrations.

Keywords
temporal trends, trace elements, Venice Lagoon

Introduction

Coastal zones, including lagoons and transitional waters are ecologically valuable systems which support a wide range of human drivers such as urbanisation and tourism, agriculture, aquaculture, industries, alteration in hydrography and substrate that lead to multiple pressures (Newton et al., 2013). Harmful elements are among the most effective environmental contaminants (Bini, 2019) and represent a major pressure affecting coastal areas (Khan et al., 2014). The aim of the present study is to investigate the occurrence of dissolved trace elements in the water of Venice Lagoon, the largest lagoon system in the Mediterranean Sea. Previous studies have been performed to investigate the level of trace metals in the lagoon of Venice figuring out the complex role played by organic ligands and dissolved/particulate partition (Morabito et al., 2018).
Many different drivers act on the Venice Lagoon ecosystem, causing multiple environmental pressures (Solidoro et al., 2010). To protect Venice and its lagoon from such natural and human-induced hazards, a legal framework consisting of a number of national laws and ministerial decrees, setting objectives, responsibilities, regulations, actions and measures has been established (Munaretto et al., 2013). Pollutants from industrial waste and other sources have been discharged to the Venice Lagoon, with a peak input during the 1960s and 1970s (Solidoro et al., 2010; Khan et al., 2014). In the framework of national laws and European Directives, census and controls of water discharges in the lagoon have been conducted and a network of water quality monitoring stations in the Venice Lagoon was established in order to evaluate the chemical status of the lagoon. In this study temporal trends of dissolved trace element concentrations in the waters, measured in the framework of the monitoring programs during campaigns spanning the decade from 2008-2017, are presented and discussed.

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Materials and methods

The monitoring of concentration levels of arsenic and trace metals in the water column of the Venice Lagoon is performed every three months by measuring the concentration of the dissolved fraction in various sampling sites (Fig. 1 and table 1).

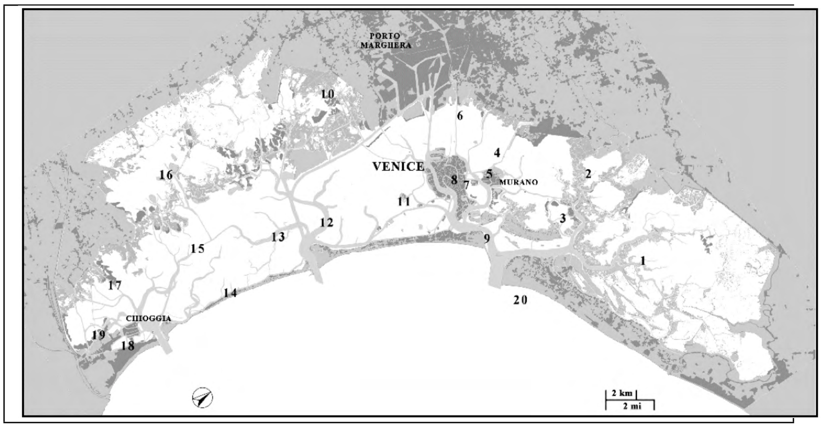

Figure 1 *Study area with the position of the sampling sites.*

Table 1. *Geographic coordinates of sampling sites*

n.	site	N	E	n.	site	N	E
1	Palude Maggiore	45°30’16.8”	12°29’17.2”	11	Sacca Sessola	45°24’09.6”	12°19’27.4”
2	Palude di Cona	45°30’25.0”	12°23’53.1”	12	Canale del Isolo	45°21’25.0”	12°18’01.3”
3	Burano	45°28’58.1”	12°25’19.2”	13	San Pietro	45°19’37.7”	12°17’01.0”
4	Campalto	45°28’10.6”	12°20’07.4”	14	Pellestrina	45°16’56.0”	12°18’04.6”
5	Murano	45°27’12.9”	12°21’21.9”	15	Settemorti	45°16’55.2”	12°15’13.4”
6	S. Giuliano	45°27’37.2”	12°17’37.0”	16	Valle Villecampi	45°17’41.5”	12°11’17.9”
7	Fondamenta Nuove	45°26’30.5”	12°20’34.8”	17	Canale Novissimo	45°13’31.8”	12°14’11.6”
8	Rialto	45°26’15.2”	12°20’05.5”	18	Laguna di Lusenzo	45°12’44.7”	12°17’16.2”
9	Lido - San Nicolò	45°25’59.7”	12°23’34.6”	19	Canale Lombardo	45°11’59.5”	12°15’54.4”
10	Lago dei Teneri	45°24’02.0”	12°12’33.4”	20	Adriatico	45°25’49.5”	12°27’25.0”

The samples were collected under neap tidal conditions at 0.5 m depth. The samples were filtered in the Class 100 laminar flow clean room by using 0.45 μm pore size filters and then acidified with ultrapure nitric acid. Concentrations of elements were measured by inductively coupled plasma mass spectrometry (ELAN DRC II, Perkin Elmer) according to method USEPA 6020B 2014. The detection limits (DL) of the dissolved fractions were 0.2 for As, 0.02 μg/L for Cd, 0.1 μg/L for Cr, Pb, Sb, V, 1 μg/L for Cu, Fe, Ni, Mn, Zn. The accuracy of the method was periodically checked by analysis of the certified reference materials SLEW-3 and CASS-6 (National Research Council of Canada).
Records were statistically analysed to identify the trends in time series data (Helsel and Hirsch, 2002; Chandler et al., 2011). Most of the data collected in this study are skewed and do not follow a normal distribution. Parametric methods may lead to misleading results in detecting differences or trends, therefore, nonparametric tests were used in this analysis (Yue et al., 2002). Non-parametric tests are commonly employed to statistically analyse series of environmental data, in particular with water quality multiple data sets that depart from normal distribution and with censored or values smaller than detection limit. Non-parametric tests do not assume that the data follow any specific distribution and are more robust to detect trends than parametric methods do (Mozejko, 2012).
Prior to conducting statistical tests, records were visually checked by scatterplots, LOWESS smooth and Box-and-whisker plots of data (Helsel and Hirsch, 2002). Correlations between records were tested using the Kendall Rank Correlation test (Kendall, 1975). The significance of seasonality was tested using Kruskal-

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Wallis test (KW) on the data grouped by season. KW test was used to data grouped by years as well. At each sampling site Mann–Kendall trend (MK) test was applied to determine whether a trend has occurred (Kendall, 1975; Hirsch et al. 1991). The null hypothesis, H_0, is that the data come from a population with independent realisations and are identically distributed. The alternative hypothesis is that the data follow a monotonic trend. Whenever the seasonal cycle was present in the data, seasonal Kendall test (SK) was applied (Hirsch and Slack, 1984). To determine whether a consistent pattern of trend occurs across the entire lagoon, at multiple locations, the Regional Kendall test for trend (RK) was applied (Helsel and Frans, 2006). Concentrations lower than detection limits were set at half of the limit. The statistical analyses performed for this study were considered significant at a p-value of less than or equal to 0.05.

Results and discussion

The Lowess smooth plots for the ten-year long term dataset are depicted in figure 2. Median, first and third interquartiles are given in table 2. Results of Regional Kendall test as significance of trend (p) and estimated rate of change (r.o.c.) are reported in table 3.

	M	Q1	Q3	min	max
As	0.91	0.70	1.24	0.10	5.5
Cd	0.022	<0.02	0.035	<0.02	1.17
Cr	0.10	<0.1	0.14	<0.1	1.16
Cu	<1	<1	<1	<1	4.3
Fe	3.4	1.9	5.9	<1	91
Mn	3.9	2.2	7.0	<1	290
Ni	1.1	<1	1.3	<1	8.1
Pb	<0.1	<0.1	<0.1	<0.1	1.0
Sb	0.21	0.17	0.26	<0.1	0.45
V	0.87	0.71	1.1	<0.5	2.6
Zn	2.6	1.4	4.4	<1	56

Table 2. *Summary statistics. M: median, Q1: first quartile, Q3: third quartile (values expressed in μg/L)*

	τ	p	r.o.c.
As	-0.18	<0.01	-0.032
Cd	-0.09	<0.01	0
Cr	-0.29	<0.01	-0.0024
Cu	-0.05	<0.01	0
Fe	+0.12	<0.01	0.15
Mn	-0.07	0.012	-0.051
Ni	-0.21	<0.01	0
Pb	-0.06	<0.01	0
Sb	-0.21	<0.01	-0.0075
V	-0.14	<0.01	-0.022
Zn	-0.35	<0.01	-0.29

Table 3. *Summary of results of Regional Kendall test for trends.* **τ**: *Kendall's tau correlation coefficient.* **p**: *significance of trend.* **r.o.c.**: *rate of change (μg/L per year).*

The Lowess smooth plots showed that most of the investigated analytes followed an irregular profile, especially evident in the central part of the plots where measurements were more dispersed, with the exception of Fe that may have had an overall increase in concentrations since 2008 but has levelled off since about 2013 and Zn that may have had a weak but steady decrease.

The median concentration of dissolved As in the Venice Lagoon was 0.91 μg/L. Higher concentrations of As were determined on the landward side of the lagoon (sampling sites 2, 4, 6, 10, 16) following a spatial distribution similar to the pattern observed in the surface sediments (Zonta et al., 2018). Kendall Rank Correlation test showed a strong correlation between records with the exception of the sampling site located

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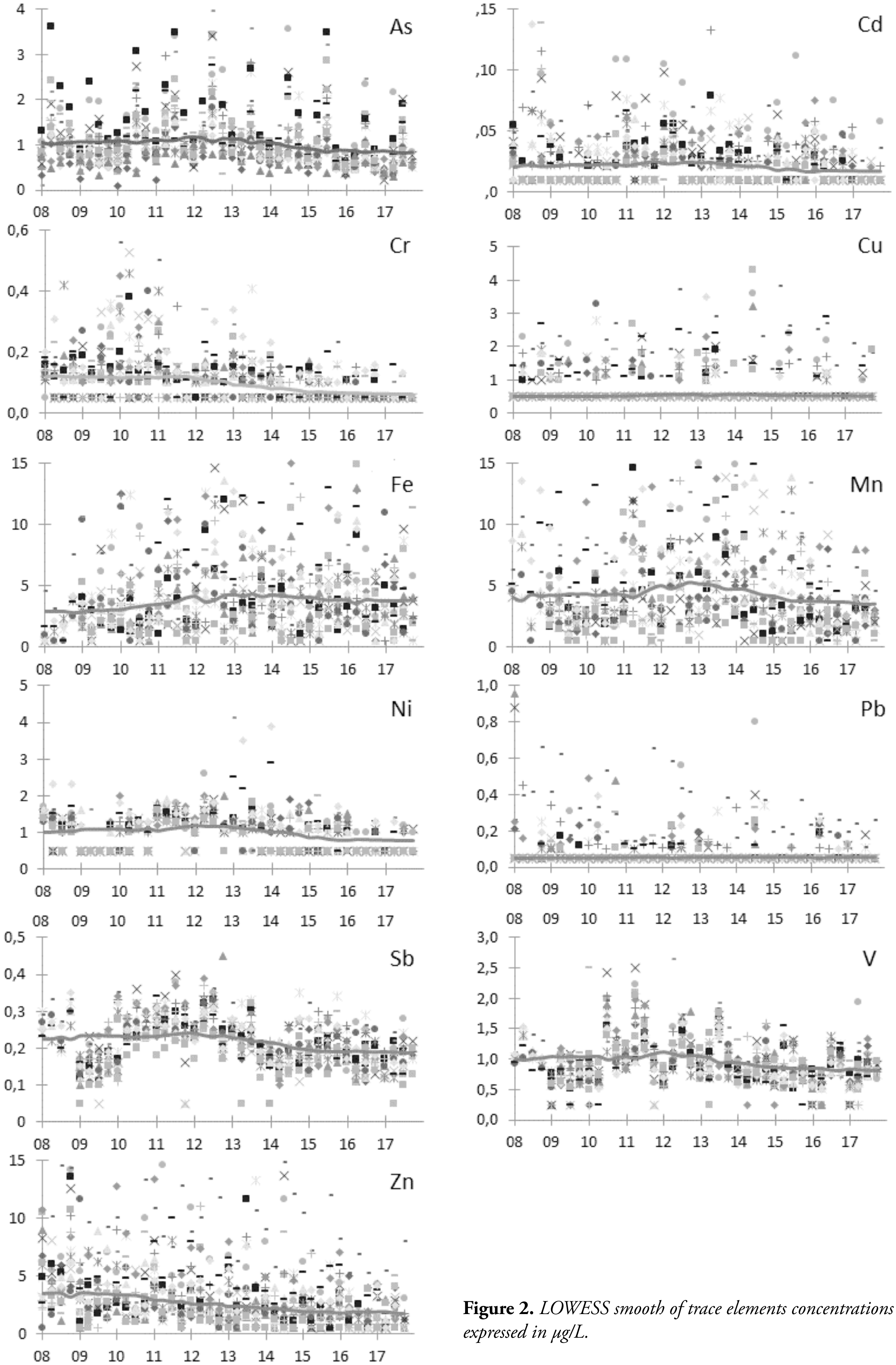

Figure 2. *LOWESS smooth of trace elements concentrations expressed in µg/L.*

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outside the lagoon (site 20) which is correlated with the site 9, do
minated by sea influence. The KW test showed there were significant differences in As concentrations when the data were grouped by season at 15 of the 20 sampling sites, with maximum concentrations occurring in the summer season and minimum occurring in winter. Differences over season were not detected at the sampling site located in the Adriatic Sea (site 20), nor at the correlated sampling sites 9. Seasonal behaviour of As has already been described in marine environment and estuaries due to natural cycling between sediments and the overlying water column and biological activity of phytoplankton (Neff, 1997). Trend tests (MK or SK) applied at each site showed a statistically significant trend at 8 records (sampling site 8, 10, 11, 12, 13, 14, 18, 19). The RK test for trend confirmed that the pattern of decreasing arsenic concentrations is statistically significant for the dataset as a whole, with a rate of change of -0.032 µg/L per year.

The concentration levels of Sb in the dissolved phase measured in the lagoon (median: 0.21 µg/L) are similar to those observed in the Adriatic Sea and comparable to the levels observed in the ocean seawater, where a median of 0.2 µg/L is reported. Sb is not considered to be highly reactive and some authors report that it behaves conservatively (Filella et al., 2002). Neither spatial pattern nor seasonal cycling were observed. At a regional scale the RK test detected a weak significant decreasing trend (p-value<0.01) with an estimated rate of change of -0.0075 µg/L per year.

Fifty percent of Cd measurements performed in the Venice Lagoon were lower than the DL. Higher concentrations were detected at the sampling sites located in the urban canals of Venice (n. 7,8) and at sampling site 6, where the percentage of measured values lower than the detection limit were 5, 10 and 28% respectively. At site 6, Cd concentrations varied with an interquartile range from less than DL to 0.060 µg/L with a median value of 0.042 µg/L. At site 7 the median value was 0.042 µg/L and the interquartile range was 0.031-0.050 µg/L. At site 8 median was 0.037 µg/L and the interquartile range was 0.025-0.052 µg/L. No seasonal pattern was clearly identified as well as no specific trend. KW test indicated a statistically significant difference in Cd concentrations among years and the RK test detected a significant decreasing trend but the estimated slope was equal to zero as a consequence of ties in the record due to the presence of a high number of values lower than the DL.

Higher concentrations of Cr were observed in the Adriatic Sea (site 20) as compared to the Venice Lagoon. Indeed, while all the values determined in the Adriatic Sea were above the DL with a median of 0.16 µg/L and an interquartile range of 0.13-0.21 µg/L, inside the lagoon 42% of Cr measurements were lower than the detection limit. The sampling sites showing higher concentrations were located close to the Lido entrance (9), with a median of 0.14 µg/L and an interquartile range of 0.11-0.17, and in the southern basin close to the urban town of Chioggia (sampling sites 18 and 19). The latter two records showed the same median value of 0.14 and similar interquartile ranges 0.11-0.16 µg/L, 0.11-0.17 µg/L respectively. The KW test did not show any significant differences in Cr concentrations when the data were grouped by season but indicated that there were statistically significant differences among years and a weak but significant decreasing trend was detected by RK test with an estimated rate of change of -0.0024 µg/L per year.

41% of Ni measurements were lower than the DL. As observed for Cr, the sampling sites with the higher percentage of measurements above the DL were 18 and 19 (24% and 21% respectively) both of them located in the southern lagoon. Medians and interquartile ranges were 1.2 µg/L, 1.0-1.5 µg/L and 1.3 µg/L, 1.0-1.6 µg/L respectively.

78% of Cu measurements were lower than the DL. The sampling site with the lowest percentage of measurements below the DL (20%) was located in the city of Venice (site 8), where a median of 1.7 µg/L and an interquartile range of 1.2-2.2 µg/L were determined. The hypothesis of no trend cannot be rejected at this site according to MK test. Even if negative trends were detected by RK test both for Ni and Cu, the estimated rates of change were equal to zero due to the presence of a high number of values lower than the DL.

As observed for Cu, most of measurements of Pb concentration (79%) were lower than the DL, with the exception of those in the site located in the urban centre of Venice (site 8) in which all values were detectable and whose median and interquartile range were 0.25 µg/L and 0.17-0.38 µg/L respectively. A significant decreasing trend was detected by MK test (p-value 0.007) at this site, with an estimated rate of change of -0.026 µg/L per year.

Concentrations of Fe in the Venice Lagoon were higher as compared to the Adriatic Sea. Median concentration of Fe in the Venice Lagoon was 3.4 µg/L with an interquartile range of 1.9-5.9 µg/L. In the Adriatic Sea (site 20) a median of 1.7 µg/L and an interquartile range of 1.1-2.6 µg/L were calculated. No seasonal pattern

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was observed when the data were grouped by season by the KW test that nonetheless indicated there were statistically significant differences in Fe concentrations among years, confirmed by the positive trend detected applying RK test, with an estimated rate of change of 0.15 µg/L per year.

As observed for Fe, concentrations of dissolved Mn measured in the Lagoon were higher than those observed in the Adriatic Sea, where a median of 1.4 µg/L was calculated. Among the sampling sites located in the lagoon those that showed higher values were 17, 18 and 19 located in the southern lagoon close to the urban town of Chioggia and site 10. Medians and interquartile ranges were: 9.1 µg/L, 4.9-16.7 µg/L (site 17), 7.5 µg/L, 4.8-14.3 µg/L (site 18), 7.0 µg/L, 4.3-13.2 µg/L (site 19) and 8.0 µg/L, 5.2-16.6 µg/L (site 10). Lower values were found at site 9 close to the seaward inlet and thus directly influenced by the Adriatic Sea, characterised by a median of 2.1 µg/L and an interquartile range of 1.2-2.6 µg/L. No seasonal pattern was clearly identified as the KW test showed significant differences in Mn concentrations when the data were grouped by season at only 5 sites out of 19 and at at site 20 (Adriatic Sea). The KW test indicated that there were statistically significant differences in Mn concentrations among years and when the analysis for trend was extended to a regional scale performing the RK test, a weak but significant decreasing trend was detected with an estimated rate of change of -0.051 µg/L per year (p-value 0.012).

Median concentration of V in the lagoon was 0.87 µg/L similar to the levels found in the Adriatic Sea (median 0.97 µg/L, first quartile 0.79 µg/L, third quartile 1.17 µg/L). The KW test showed there were significant differences in V concentrations when the data were grouped by season at 9 of the various sampling sites, with maximum concentrations occurring in the summer season and minimum in winter. The seasonal pattern was detected mainly at the sampling sites located on the landward side of the lagoon. Higher levels of dissolved vanadium under summer conditions have also been reported in coastal systems as a consequence of water-particle interaction and biological activity of phytoplankton (Wang et al., 2009). A weak but significant decreasing trend was detected by RK test with an estimated rate of change of -0.022 µg/L per year (p-value <0.01).

Turning now to Zn, median concentration in the Venice Lagoon was 2.6 µg/L, first and third quartile were 1.4 µg/L and 4.4 µg/L respectively, whereas in the Adriatic sea Zn concentrations varied with an interquartile range from less than DL to 2.8 µg/L with a median of 1.2 µg/L. Higher concentrations were determined in the sampling site located inside the centre of Venice, where a median of 8.9 µg/L and an interquartile range of 6.8-11.1 µg/L were calculated, indicating an urban source for this element. The KW test did not show any significant differences in Zn concentrations when the data were grouped by season. The MK test applied at each site showed a statistically significant trend for all of records and KW test indicated that there were statistically significant differences in Zn concentrations among years. When the analysis for trend was extended to a regional scale performing the RK test, a significant decreasing trend was detected with an estimated rate of change of -0.29 µg/L per year. Two further points characterised by higher level of Zn were 6 and 10 (median: 4.4 µg/L, 4.6 µg/L; interquartile range: 2.3-6.7 µg/L, 2.4-7.5 µg/L respectively). In the same areas higher concentrations of Zn in the surface sediments has been reported and a significant enrichment in Zn in the surface more recent lagoon sediments, as compared to the deeper pre-industrial sediments, has been described as well (Zonta et al., 2018).

The spatial distribution and vertical profile of Zn in sediments is a consequence of anthropogenic inputs in the Venice Lagoon and may have their origin in industrial activities such as the sphalerite ore processing plant that operated in the last century. Sewage effluent, road runoff and antifouling paints have also been described as sources of Zn in marine environments (Lagerström et al., 2018). An additional source of Zn are sacrificial anodes frequently used in ships and boats (Rees et al. 2017) and ballast water tanks (Jelmert and van Leewen, 2000). The Venice Lagoon is home to thousands of boats. Moreover, thousands of commercial vessels and cruise ships navigate through the lagoon channels in a given year. Corrosion is a general problem for offshore infrastructures too and cathodic systems are the most commonly used techniques to prevent corrosion (Kirchgeorg et al., 2018). At the seaward inlets that connect the lagoon to the Adriatic Sea, a system designed to prevent the city of Venice from being flooded by the sea consisting of steel gates (Eprim, 2005) is in the final stages of construction. For the protection from corrosion of this huge amount of steel with a corresponding large exposed surface inside and outside the barriers, a cathodic protection system based on sacrificial zinc anodes have been used. At the anodes vicinity, the suspended particles matter and dissolved fraction of surrounding marine waters is expected to be enriched of metals (Deborde et al., 2015) even

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if after the anode activation period, the metal inputs from galvanic anode dissolution are rapidly diluted by seawater renewal and these metal fluxes should be negligible (Deborde et al., 2015). Even if anomalies were not currently detected in the levels of Zn at the seaward inlets, in the light of these considerations, the Zn concentrations in the waters of the lagoon must be carefully monitored in the following years, as well as analysed for trends. The spatial variability and seasonal variations of chemical parameters such as As and other trace elements is linked to the complex morphology and the irregular hydrology of the lagoon that make it similar to a mosaic pattern of various parts with different characteristics (Ravera et al., 2000). The detectable levels of Cu and Pb and the higher concentrations of Zn observed in the city of Venice, are reflected by the very high levels observed in the sediments of the city's canal network as compared to areas all around the city. This is probably due to the limited hydrodynamics of the canal network that increase the retention of pollutants (Zonta et al., 2018). Higher concentrations of elements, in particular for As, Cd and Zn, were also determined in waters of the industrial canals of Porto Marghera, located on the western shore of the Venice Lagoon, as compared to the lagoon. Median values in the industrial canals for dissolved As, Cd, Cr, Cu, Fe, Pb and Zn were 1.7, 0.04, 0.11, 1.15, 3.0, 0.1, 6.0, respectively (Berti et al., 2018). The resuspension of contaminated sediments stored in the canals of the industrial area represents the major potential source of contaminants to the lagoon (Bellucci et al., 2002). The modelling results of the source apportionment suggests that the contaminant enrichment in the water column via resuspension of upper sediments in the central basin, including the industrial and urban areas, may circulate in the lagoon, in particular in the northern and central basin (Sommerfreund et al., 2010).

Conclusions

As far as the median levels of arsenic and metals are concerned, the Venice Lagoon waters showed a relatively low contamination as compared to ranges reported for other industrialised coastal systems (e.g. Hatje et al., 2003; Cuong et al., 2008, and literature therein). The time series analysis in the last decade revealed that the concentrations of arsenic and heavy metals have been constant or have showed a decreasing trend, with the exception of iron. The Venice Lagoon has a long history of extensive human intervention covering about ten centuries (Ravera, 2000). This uninterrupted work has been undergoing until the present days. According to Ferrarin et al. (2013) the periodical closure of the lagoon from the sea during flooding events and the sea level rise are expected to modify the hydrological condition. The ensuing changes in the water renewal time may affect the cycling, mobility and fate of trace elements in the lagoon whose levels and trends need careful monitoring in the future.

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References

BELLUCCI L. G., FRIGNANI M., PAOLUCCI D., RAVANELLI M. (2002) Distribution of heavy metals in sediments of the Venice Lagoon: the role of the industrial area, Science of The Total Environment, 295:35-49.

BERTI M., BERTINI S., VOLPATO E., CARRER C., DALLA PALMA M., SORRENTINO F. (2018) Temporal trends of trace elements in waters of the industrial canals in Porto Marghera (Venice, Italy), EQA – Int. Jour. of Environ. Qual., 29:67-76.

BINI C. (2019). Urban soils and human health, EQA – Int. Jour.of Environ. Qual., 33:1-10.

CHANDLER R. E., SCOTT E. M. (2011) Statistical Methods for Trend Detection and Analysis in the Environmental Sciences, John Wiley & Sons Ltd, Chichester (UK).

CUONG D. T., KARUPPIAH S., OBBARD J. P. (2008) Distribution of heavy metals in the dissolved and suspended phase of the sea-surface microlayer, seawater column and in sediments of Singapore's coastal environment, Environmental Monitoring and Assessment, 138:255-272.

DEBORDE J., REFAIT P., BUSTAMANTE P., CAPLAT C., BASUYAUX O., GROLLEAU A. M., MAHAUT M. L., BRACH-PAPA C., GONZALEZ J. L., PINEAU S. (2015) Impact of Galvanic Anode Dissolution on Metal Trace Element Concentrations in Marine Waters, Water, Air, & Soil Pollution, 226-423.

EPRIM, Y. (2005) Venice mobile barriers project: Barrier caissons construction details. In: Fletcher C. A., Spencer T. (Ed.), Flooding and environmental challenges for Venice and its Lagoon: State of Knowledge, Cambridge University Press, Cambridge, 257-265.

DOI: 10.6092/issn.2281-4485/9530

FERRARIN C., GHEZZO M., UMGIESSER G., TAGLIAPIETRA D., CAMATTI E., ZAGGIA L., SARRETTA A. (2013) Assessing hydrological effects of human interventions on coastal systems: numerical applications to the Venice Lagoon, Hydrology and Earth System Sciences, 17:1733-1748.

FILELLA M., BELZILE N., CHEN Y. W. (2002) Antimony in the environment: a review focused on natural waters I. Occurrence, Earth-Science Reviews 57:125–176.

HATJE V., APTE S. C., HALES L. T., BIRCH G. F. (2003) Dissolved trace metal distribution in Port Jackson estuary (Sydney Harbour), Australia, Marine Pollution Bulletin, 46:719-730.

HELSEL D. R., HIRSCH R. M. (2002) Statistical methods in water resources. In: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 4 Hydrologic Analysis and Interpretation. U.S. G.S.

HELSEL D., FRANS L. M. (2006) Regional Kendall Test for Trend, Environmental Science & Technology, 40(13):4066-4073.

HIRSCH R. M., SLACK J. R. (1984) A Nonparametric Trend Test for Seasonal Data With Serial Dependence, Water Resources Research, 20:727-732.

HIRSCH R. M., ALEXANDER R. B., SMITH R. A. (1991) Selection of methods for the detection and estimation of trends in water quality.Water resources research,27(5):803-813.

JELMERT A., VAN LEEUWEN J. H. (2000) Harming local species or preventing the transfer of exotics? Possible negative and positive effects of using zinc anodes for corrosion protection of ballast water tanks, Water Research, 34:1937-1940.

KENDALL M. G. (1975) Rank correlation methods, 4th Ed., Charles Griffin, London.

KHAN M. B., MASIOL M., HOFER A., PAVONI B. (2014) Harmful Elements in Estuarine and Coastal System, In: BINI C., BECH J. (Ed.), PHEs, Environment and Human Health, Springer, Dordrecht, 37-83.

KIRCHGEORG T., WEINBERG I., HÖRNIG M., BAIER R., SCHMID M. J., BROCKMEYER B. (2018) Emissions from corrosion protection systems of offshore wind farms: Evaluation of the potential impact on the marine environment, Marine Pollution Bulletin, 136:257-268.

LAGERSTRÖM M., LINDGREN J. F., HOLMQVIST A., DAHLSTRÖM M., YTREBERG E. (2018) In situ release rates of Cu and Zn from commercial antifouling paints at different salinities, Marine Pollution Bulletin 127:289–296.

MORABITO E., RADAELLI M., CORAMI F., TURETTA C., TOSCANO G., CAPODAGLIO G. (2018) Temporal evolution of cadmium, copper and lead concentration in the Venice Lagoon water in relation with the speciation and dissolved/particulate partition, Marine Pollution Bulletin, 129:884-892.

MOZEJKO J. (2012). Detecting and Estimating Trends of Water Quality Parameters. In: Dr. VOUDOURIS (Ed.), Water Quality Monitoring and Assessment, InTech, 95-120.

MUNARETTO S., VELLINGA P., TOBI H. (2012) Flood Protection in Venice under Conditions of Sea-Level Rise: An Analysis of Institutional and Technical Measures, Coastal Management, 40:355-380.

NEFF J.M. (1997) Ecotoxicology of arsenic in the marine environment, Environmental Toxicology and Chemistry, 16:917–927.

NEWTON A., ICELY J., CRISTINA S., BRITO A., CARDOSO A. C., COLIJN F., DALLA RIVA S., GERTZ F., HANSEN J. W., HOLMER M., IVANOVA K., LEPPÄKOSKI E., MELAKU CANU D., MOCENNI C., MUDGE S., MURRAY N., PEJRUP M., RAZINKOVAS A., REIZOPOULOU S., PÉREZ-RUZAFA A., SCHERNEWSKY G., SCHUBERT H., CARR L., SOLIDORO C., VIAROLI P., ZALDÍVAR J. M. (2014) An overview of ecological status, vulnerability and future perspectives of European large shallow, semi-enclosed coastal systems, lagoons and transitional waters, Estuarine, Coastal and Shelf Science, 140:95-122.

RAVERA O. (2000) The Lagoon of Venice: the result of both natural factors and human influence, Journal of Limnology, 59(1):19-30.

REESE A. B., GALLAGHER A., COMBER S., WRIGHT L. A. (2017) An analysis of variable dissolution rates of sacrificial zinc anodes: a case study of the Hamble estuary, UK, Environmental Science and Pollution Research 24(26):21422–21433.

SOLIDORO C., BANDELJ V., AUBRY BERNARDI F., CAMATTI E., CIAVATTA S., COSSARINI G., FACCA C., FRANZOI P., LIBRALATO S., MELAKU CANU D., PASTRES R., PRANOVI F., RAICEVICH S., SOCAL G., SFRISO A., SIGOVINI M., TAGLIAPIETRA D., TORRICELLI P. (2010) Response of the Venice Lagoon Ecosystem to Natural and Anthropogenic Pressures over the Last 50 Years, In: Kennish M. J., Paerl H. W. (Ed.), Coastal Lagoons: Critical Habitats of Environmental Change, CRC Press, Boca Raton FL, 483-511.

DOI: 10.6092/issn.2281-4485/9530

SOMMERFREUND J.K., GANDHI N., DIAMOND M.L., MUGNAI C., FRIGNANI M., CAPODAGLIO G., GERINO M., BELLUCCI L. G., GIULIANI S. (2010) Contaminant fate and transport in the Venice Lagoon: Results from a multi-segment multimedia model, Ecotoxicology and Environmental Safety, 73(3):222-230.

USEPA Method 6020B (2014) Inductively coupled plasma-mass spectrometry. In: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods SW-846, U.S. EPA, Washington DC.

WANG D, SAÑUDO WILHELMY S. A. (2009) Vanadium speciation and cycling in coastal waters, Marine Chemistry 117:52–58.

YUE S., PILON P., CAVADIAS G. (2002) Power of the Mann-Kendall and Spearman's rho tests for detecting monotonic trends in hydrological series, Journal of Hydrology, 259(1-4):254-271.

ZONTA R., BOTTER M., CASSIN D., BELLUCCI L. G., PINI R., DOMINIK J. (2018) Sediment texture and metal contamination in the Venice Lagoon (Italy): A snapshot before the installation of the MOSE system, Estuarine, Coastal and Shelf Science, 205:131-151.

VARIABILITÉ SPATIALE ET ÉVOLUTION TEMPORELLE DES OLIGO-ÉLÉMENTS DISSOUS DANS LES EAUX DE LA LAGUNE DE VENISE (ITALIE)

Resumé

Une enquête visant à évaluer la variabilité spatiale et l'évolution temporelle des eaux de la lagune de Venise a permis d'obtenir un ensemble complet de données sur les concentrations d'oligo-éléments dissous pendant une décennie (2008-2017) - données recueillies au cours de campagnes de surveillance. Les niveaux de concentration aux différents sites révèlent que la lagune n'est pas homogène, mais un système composé de différentes zones ayant des caractéristiques différentes dûes aux diverses sources de polluants. Toutefois, l'analyse de tendance effectuée à la fois sur chaque site et sur l'ensemble de la lagune a révélé que l'arsenic et les métaux lourds présentent peu de variations ou de tendances décroissantes, à l'exception du fer qui peut avoir connu une augmentation globale des concentrations.

Mots-clés: *tendances temporelles, oligo-éléments, lagune de Venise*

VARIABILITÀ SPAZIALE ED EVOLUZIONE TEMPORALE DEGLI ELEMENTI IN TRACCE DISCIOLTI NELLE ACQUE DELLA LAGUNA DI VENEZIA (ITALIA)

Riassunto

Al fine di valutare la variabilità spaziale e l'evoluzione temporale delle concentrazioni di elementi in tracce nelle acque della laguna di Venezia, sono state studiate le serie storiche comprese nel periodo 2008-2017. I livelli di concentrazione nei diversi siti rivelano come la laguna sia tutt'altro che un sistema omogeneo essendo costituita da corpi idrici con caratteristiche differenti e diverse sorgenti di inquinanti, mentre sia l'analisi delle tendenze eseguite ad ogni sito sia l'analisi estesa all'intera laguna mostrano che i livelli di concentrazione dell'arsenico e dei metalli pesanti hanno subito nel tempo piccole variazioni o andamenti decrescenti, ad eccezione del ferro che sembra mostrare un generale incremento.

Parole chiave: *andamenti temporali, elementi in tracce, laguna di Venezia*